# Acoustic Probing of Phase Equilibria in Near Critical Fluids

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## **KEYWORDS**

experimental method, critical state, vapor-liquid equilibria

### **ABSTRACT**

Phase behavior is a fundamental aspect of supercritical fluids. We describe a simple acoustic method for the investigation of fluid phase equilibria. The method is used to investigate pure components, binary and ternary mixtures. In contrast to highly accurate speed of sound measurements in homogeneous fluids, we investigate the vapor-liquid boundaries of mixtures. The reciprocal of the speed of sound was measured at selected near-critical isotherms. For mixtures isopleths are measured to establish the course of the critical line. All data for pure components are in good agreement with the literature where available. Limitations of the acoustic method in determining phase equilibria are discussed.

## INTRODUCTION

Over the last decade, supercritical mixtures have become increasingly attractive for new industrial processes. However, reaction mixtures have to be homogeneous to exploit the advantages of supercritical fluids. Therefore, the phase envelopes of the systems have to be known to maintain homogenity. Measurements of phase envelopes are usually performed by visual methods or by sampling (Schneider, 1983). Unfortunately, both methods have disadvantages. Accurate sampling is difficult especially for highly dilute mixtures. Additionally, analytical methods have a poor performance in obtaining critial data and are not applicable to equilibria with more than two fluid phases.

Visual methods are superior to analytical techniques for obtaining critical data, but the

determination of a critical point is constrained by the subjectivity of the experimenter. Our acoustic method overcomes the disadvantages of both sampling and visual methods. Firstly, it is applicable to nearly all types of fluid phase behavior. Secondly, all measurements are made in a totally opaque vessel, and hence, are completely objectively. Thirdly, vapor-liquid phase transitions and critical points can be easily recognized by a pronounced minimum in the speed of sound.

The key property in acoustic measurements is compressibility (Rowlinson and Swinton, 1982), which reaches a maximum whenever a phase transition occurs. Compressibility i related to the speed of sound and, hence, by measuring the variation in the speed of sound in a particular system, the phase envelope of that system can be obtained.

Over the last 25 years, several authors have reported high precision speed of sound measurements of pure fluids and binary mixtures. Most of these experiments were carried out with spherical resonators which have a superior signal to noise ratio to other cell geometries (Moldover et al., 1979) (Mehl, 1982 and 1985) (Colgate et al., 1991) (McElroy, 1995).

Surprisingly, no one has used the acoustic technique to obtain information about phase boundaries in the way reported here. Presumably, researchers were deterred by problems such as the complex cell geometry and effects of precondensation or bubble formation either from homogeneous gas or liquid phases. Nevertheless, we have been able to reproduce critical points for pure components with a very simple cell design. These results encouraged us to work on mixtures.

Our initial investigations involved refrigerant mixtures. These mixtures exhibit particularly small density differences between the coexisting phases, and are therefore difficult to measure either visually or analytically. With our apparatus we were able to

determine the critical loci of several binary systems containing refrigerants (Kordikowski et al, 1996a). We then investigated a variety of other binary and ternary mixtures. The components varied from permanent gases and refrigerants to edible oils. The results have proved that critical data can be obtained as easily for multi component mixtures as for pure substances (Kordikowski et al., submitted). The results in this paper show that azeotropy is also detectable. Nevertheless the acoustic determination of phase equilibria also has some disadvantages. The depth of the minimum in the speed of sound at the phase transition is dependent on the number of components in the mixture and on their physical properties. An increasing proportion of permanent gas decreases the depth of the minimum until it almost disappears (Kordikowski et al., submitted), and liquid-liquid critical points are as yet undetectable with the current set-up of our equipment. Despite these limitations, the acoustic method is already providing information about systems for which other methods cannot provide reliable data.

# **EXPERIMENTAL SECTION**

The acoustic cell is constructed from two standard stainless steel 1/4-inch-cross-pieces, to provide an acoustic cavity of about 4 ml volume. A schematic representation of the experimental equipment is shown in Fig. 1. A detailed description of the experimental setup and the filling procedure has already been given elsewhere (Kordikowski et al., 1996a). Pressure was constant within  $\pm$  0.1 bar and temperature within  $\pm$  0.02 K. The acoustic cell was thermostated with an aluminum jacket. The acoustic signal was provided by a pulse generator, which produced a microsecond ultrasonic pulse with a frequency of 0.5 MHz. The resulting signal was amplified and displayed on an oscilloscope.

## RESULTS AND DISCUSSION

# **Pure Components**

Acoustic measurements were carried out with several pure components to validate the data from our technique. For each component, several isotherms around the critical temperature were measured. The results for  $C_2H_6$  are shown as an example in Fig. 2. It can be seen that the time delay increases as the sample approaches its critical point. Although, the temperature difference between the isotherms is only 0.1 K, the critical isotherm can easily be distinguished from its neighbors. Within the error of our equipment, the measured critical point is identical to the literature p = 48.7 bar and T = 305.35 K (Moldover and Gallagher, 1978).

### **Mixtures**

Differences in composition should lead to differences in the acoustic properties of a mixture. To check the applicability of our new equipment, we measured a variety of mixtures, especially ones containing  $CO_2$ ,  $C_2H_6$  and refrigerants. Critical curves of systems containing  $CO_2$  or  $C_2H_6$ , measured with our equipment are shown in their p,T-projection in Fig. 3. All of the systems exhibit a so-called Type I fluid phase behavior with the exception of  $CO_2$  + He, which shows gas-gas immiscibility of the first kine (Tsiklis, 1952). In all cases except  $CO_2$  + He we were able to cover the whole mole fraction range.

Our first major study involved mixtures of partially fluorinated gases with  $CO_2$  or  $C_2H_6$ . Mixtures of these gases can be used as refrigerants or as modifiers for supercritical chromatography and extraction. Therefore, knowledge of their phase behavior is

important. These systems are difficult to measure visually, because density differences between the coexisting phases are small even a long way from the critical point. With our acoustic technique, we were able to determine the critical lines of a variety of systems over the whole composition range. As expected, all systems with refrigerants CHF $_3$  (R23), CH $_2$ F $_2$  (R32), CF $_3$ CH $_2$ F (R134a) show Type I fluid phase behavior, with a continuous critical line. Nevertheless, there are some striking differences between their shapes of the critical curve for CO $_2$  / R134a and C $_2$ H $_6$  / R134a, due to hydrogen bonding (Kordikowski et al., 1996a).

Our second interest has been the investigation of the behavior of the acoustic signal in mixtures with permanent gases. In the system  $CO_2$  + He, we showed that we could detect effects due to minute amounts of He dissolved in  $CO_2$  withdrawn from gas cylinders overpressured with He. The mole fraction of He ranges only from x(He) = 0.001-0.03. Nevertheless, changes in the critical pressure were easily detected by our acoustic method. We showed that there is a substantial variation in the content between individual He-Head-Pressure-Cylinders, depending on their filling date (Kordikowski et al, 1996b), indicating that those cylinders are not necessarily in thermodynamic equilibrium.

Additionally, systems containing CO were investigated to quantify the effect of larger amounts of a permanent gas on the acoustic signal. We shave found that the maximum in transit time becomes increasingly shallow and vanishes when the mole fraction of permanent gas is raised (Kordikowski et al., submitted).

We have now extended our studies to two ternary systems. One contained  $CO_2$  and two refrigerants the other CO and two alkanes. For these systems, the ternary critical surface was explored with quasibinary mixtures. We investigated several quasibinary mixtures

for both ternary systems to ensure that the rest of the ternary critical surface could be predicted. The ternary data were plotted in a so-called p,T,x<sup>red</sup>-phase cube as proposed by (Kordikowski and Schneider, 1993). This method enables the experimenter to visualize the entire critical surface and predict its shape even in areas where no experiments can be done.

Very recently we have started investigating the system  $C_2H_6 + CHF_3$ . This binary system is interesting because it exhibits absolute positive azeotropy. Many years ago Thorp and Scott (1956) showed that this system shows liquid-liquid immiscibility combined with heteroazeotropy, resulting in a Type II-HA phase behavior. The binary critical line the azeotropic line and the vapor pressure curves are shown in Fig. 4. The calculated vapor pressure curves show a Bancroft Point at 262 K, which is not shown in Fig. 4. As can be seen from Fig. 4 the differences between the critical pressures are very small. The system is similar to  $CO_2 + C_2H_6$  (Ohgaki and Katayama, 1977), but total pressure difference in the whole binary critical curve is less than 2.5 bars. The critical curve shows a temperature minimum at 284.2 K and a pressure minimum at 46.5 bar. We have located the azeotropic critical point atx( $C_2H_6$ ) = 0.47, p = 46.6 bar and T = 284.4 K.

Currently we are investigating the ternary system  $CO_2 + C_2H_6 + CHF_3$ . The ternary system contains two binary azeotropes. This should lead to an azeotropic critical end point (ACEP) in the ternary system, in which two different ternary critical lines meet. The interesting results will be diplayed in a p,T,x<sup>red</sup>-phase cube to envisage the complicated shape of the ternary critical surface.

# **CONCLUSION**

We have shown that our simple acoustic equipment can be used to determine liquid-vapor equilibrium data for pure components. The deviations between literature and measured data for pure components are within the experimental error of our equipment. Vapor-liquid equilibria and critical points for binary and ternary systems could also be measured without difficulties. Also mixtures which show almost no difference in bubble and dew point pressures (refrigerant mixtures), and mixtures with trace amounts of a permanent gas (He mixtures) can be successfully investigated. We have shown that the acoustic method is a reliable and fast method for the determination of fluid phase equilibria, independent of the nature of the fluid. It has wide applicability and provides an objective method for obtaining data points, making it preferable to optical techniques for many applications.

### ACKNOWLEDGEMENTS

We thank the British Council, the EPSRC Clean Technology Unit, the Royal Academy of Engineering, BP Chemicals Ltd and the Alexander von Humboldt-Foundation for financial support. We are grateful to Professor V. N. Bagratashvili, Professor M. Nunes da Ponte, Dr. M. W. George, Dr. A. Aguiar-Ricardo, N. R. A. Ribeiro, D. G. Robertson and Dr. V. N. Popov for their help and advice. We thank Mr. M. Guyler and Mr. K. Stanley for technical support.

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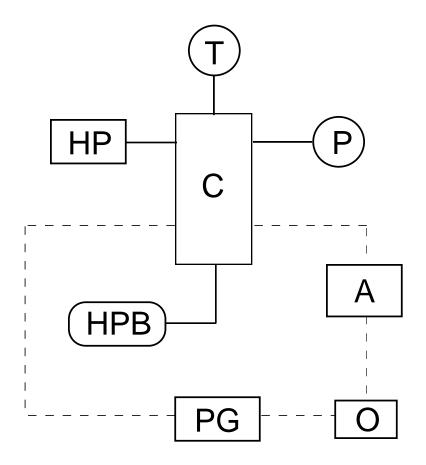
## FIGURE CAPTIONS

Fig. 1: Schematic view of the acoustic apparatus. Components are labeled as follows: A, Amplifier; C, Acoustic Cell; HP, Hand Pump; HPB, High Pressure Bomb; O, Oscilloscope; P, Pressure Transducer; PG, Pulse Generator; T, Thermocouple.

Fig. 2: Time delay (μs) versus pressure for near-critical isotherms of pure C<sub>2</sub>H<sub>6</sub> in the temperature range 305.15 K - 305.65 K. Subcritical isotherms are marked with filled black symbols, supercritical isotherms with outline symbols and the critical isotherm with a center-dotted circle.

Fig. 3: P,T-projection of binary critical lines determined with our acoustic equipment. Open squares represent the critical points of the pure components. The binary systems are represented by the following symbols,  $\circ$  CO<sub>2</sub> + CH<sub>2</sub>F<sub>2</sub>,  $\square$  CO<sub>2</sub> + CF<sub>3</sub>CH<sub>2</sub>F,  $\triangle$  CO<sub>2</sub> + CHF<sub>3</sub>,  $\blacklozenge$  CO<sub>2</sub> + He,  $\blacktriangledown$  C<sub>2</sub>H<sub>6</sub> + CF<sub>3</sub>CH<sub>2</sub>F.

Fig. 4: P,T-projection of the system  $C_2H_6 + CHF_3$ . Open symbols  $\triangle$  represent binary critical data. The dashed line with full diamonds  $\bullet$  represents the binary azeotropic curve. Full symbols  $\bullet$  and  $\blacksquare$  represent calculated vapor pressure data (Reid, Prausnitz and Poling, 1987).



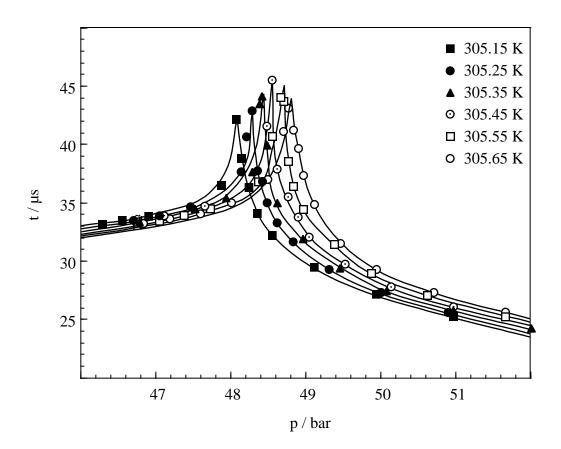


Fig. 2 A. Kordikowski and M. Poliakoff Acoustic Probing of Phase Equilibria in Near Critical Fluids

